Kohlraushc law on independent migration of ions

It depend only ∞-dilution

It is applicable both strong & weak electrolyte.

At infinite dilution dissociation of electrolyte is complete then each ion make a definite contribution towards equivalent conductance of electrolyte irrespective of other ion

It's law state that, at ∞-dilution

Equivalent Conductance of electrolyte is sum of equivalent Conductance of Cation and anion at ∞-dilution

Kohlrausch law

Ex:- $A_xB_y \longrightarrow xA^{+y} + yB^{-x}$

V.f. of A_xB_y $= xy$

$$\lambda^{\infty}_{eq(A_xB_y)} = \lambda^{\infty}_{eq(A^{+y})} + \lambda^{\infty}_{eq(B^{-x})}$$

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$$\Lambda_{eq}^{\infty} = \frac{\Lambda_m^{\infty}}{V.f.} \Rightarrow \Lambda_m^{\infty} = \Lambda_{eq}^{\infty} \cdot V.f.$$

$$\Lambda_{m(A_xB_y)}^{\infty} = \Lambda_{eq(A_xB_y)}^{\infty}\, xy$$

given

Molar Conductance of cation $(A^{+y}) = \Lambda_{m(A^{+y})}^{\infty}$

Molar conductance of anion $(B^{-x}) = \Lambda_{m(B^{-x})}^{\infty}$

$$\Lambda_{eq(A_xB_y)}^{\infty} = ?$$

$$\lambda^{\infty}_{eq(A^{+y})} = \frac{\lambda^{\infty}_{m(A^{+y})}}{y} \quad ; \quad y = \text{v.f. of cation (charge on cation)}$$

$$\lambda^{\infty}_{eq(B^{-x})} = \frac{\lambda^{\infty}_{m(B^{-x})}}{x} \quad ; \quad x = \text{V.f. of anion (charge on anion)}$$

$$\boxed{\lambda^{\infty}_{eq(A_xB_y)} = \frac{\lambda^{\infty}_{m(A^{+y})}}{y} + \frac{\lambda^{\infty}_{m(B^{-x})}}{x}}$$

equivalent conductance of A_xB_y in terms of Molar Conductance.

Ques. Limiting ionic conductance (Conductance at ∞ dilution) of H^+ & SO_4^{2-} are 360 $S\,cm^2\,eq^{-1}$ & 80 $S\,cm^2\,eq^{-1}$ respectively. Cal. equivalent & molar conductance of H_2SO_4 at ∞-dilution.

$V.f = 2$

Sol given:

$$\Lambda_{eq}^{\infty}(H^+) = 360\ S\,cm^2\,eq^{-1}$$

$$\Lambda_{eq}^{\infty}(SO_4^{2-}) = 80\ S\,cm^2\,mol^{-1}$$

$$\Lambda_{eq}^{\infty}(H_2SO_4) = 360 + 80 = 440$$

$$\Lambda_m^{\infty}(H_2SO_4) = 440 \times 2 = 880$$

Q.2. limiting ionic conductance of Al^{+3} & SO_4^{2-} ion are 189 $S\,cm^2\,mol^{-1}$ & 160 $S\,cm^2\,mol^{-1}$

Cal equivalent & molar conductance of $Al_2(SO_4)_3$ at ∞ - dilution.

V.F. = 6

Sol - given - $(2Al^{+3} + 3SO_4^{2-})$

$\lambda_m^{\infty}(Al^{+3}) = 189\ S\,cm^2\,mol^{-1}$

$\lambda_{eq}^{\infty}(Al^{+3}) = \frac{189}{3} = 63\ S\,cm^2\,eq^{-1}$

$\lambda_m^{\infty}(SO_4^{2-}) = 160\ S\,cm^2\,mol^{-1}$

$\lambda_{eq}^{\infty}(SO_4^{2-}) = \frac{160}{2} = 80$

$\lambda_{eq}^{\infty}\,Al_2(SO_4)_3 = 63 + 80 = 143$

$\lambda_m^{\infty}\,Al_2(SO_4)_3 = 143 \times 6$

$= 858\ S\,cm^2\,mol^{-1}$

Applications of Kohlrausch law :

(1) To deter molar conductance of weak electrolyte

Ex : (i) $\Lambda_m^\infty(NH_4OH) = ?$

given

$\Lambda_m^\infty(NH_4Cl) = a$

$\Lambda_m^\infty(NaOH) = b$

$\Lambda_m^\infty(NaCl) = c$

$\Lambda_m^\infty(NH_4OH) = \Lambda_m^\infty(NH_4^+) \; \Lambda_m^\infty(OH^-)$

Target

$$\Lambda_m^{\infty}(NH_4Cl) = \Lambda_m^{\infty}(NH_4^+) + \Lambda_m^{\infty}(Cl^-) \quad \text{— (1)}$$

$$\Lambda_m^{\infty}(NaOH) = \Lambda_m^{\infty}(Na^+) + \Lambda_m^{\infty}(OH^-) \quad \text{— (2)}$$

$$\Lambda_m^{\infty}(NaCl) = \Lambda_m^{\infty}(Na^+) + \Lambda_m^{\infty}(Cl^-) \quad \text{— (3)}$$

Eq (1) + (2) − (3)

$$\Lambda_m^{\infty}(NH_4OH) = \Lambda_m^{\infty}(NH_4Cl) + \Lambda_m^{\infty}(NaOH) - \Lambda_m^{\infty}(NaCl)$$

$$\boxed{\Lambda_m^{\infty}(NH_4OH) = a + b - c}$$

Ex: (ii) $\Lambda_m^\infty Ba(OH)_2 = ?$

given: $\Lambda_m^\infty BaCl_2 = x$ — (1)

$2 \times \Lambda_m^\infty (NaOH) = y$ — (2)

$2 \times \Lambda_m^\infty (NaCl) = Z$ — (3)

eq (1) + 2 eq (2) − 2 × eq (3)

$$\Lambda_m^\infty Ba(OH)_2 = \Lambda_m^\infty Ba^{2+} + 2\Lambda_m^\infty (OH^-)$$

$$\Lambda_m^\infty Ba(OH)_2 = x + 2y - 2Z$$

(2) To determine degree of dissociation (α) of weak electrolyte –

$$\boxed{\alpha = \frac{\lambda_{eq}}{\lambda_{eq}^{\infty}}} = \frac{\lambda_m / \cancel{v.f}}{\lambda_m^{\infty} / \cancel{v.f}}$$

OR

$$\boxed{\alpha = \frac{\lambda_m}{\lambda_m^{\infty}}}$$

(3) To determine dissociation constant (K_a or K_b) :-

for weak acid, $K_a = \frac{C\alpha^2}{1-\alpha}$

for weak base, $K_b = \frac{C\alpha^2}{1-\alpha}$

* If $\alpha << 1$ then $1-\alpha \approx 1$

$$K_a / K_b = C\alpha^2$$

(4) To determine Solubility (S) & Solubility product (K_{sp})

molar conc. of saturated soln is k/a solubility.

Saturated soln of sparingly soluble salt is considered at inifinite dilution

for saturated soln

$M \rightarrow S$

$\Lambda_m \rightarrow \Lambda_m^\infty$

$$\boxed{\Lambda_m^\infty = \frac{K \cdot 1000}{S}}$$

$S \rightarrow$ Solubility

Ksp of AB typeelectrolyte-

$$AB_{(s)} \longrightarrow A^{+}_{(aq)} + B^{-}_{(aq)}$$

$$\qquad\qquad\qquad S \qquad S$$

$$\boxed{K_{sp} = S^2}$$